Steric Consequences on the Conformation of Medium-Sized Rings: Solution NMR, Solid-State Crystallographic, *ab Initio* Molecular Orbital Calculations, and Molecular Mechanics Studies on Substituted Eight-Membered Organosilicon Ring Systems¹

Lilibeth P. Burke,[†] Anthony D. DeBellis,[‡] Herman Fuhrer,[§] Hansrudolf Meier,^{*,||} Stephen D. Pastor,^{*,‡} Grety Rihs,[§] Guenther Rist,[§] Ronald K. Rodebaugh,[†] and Sai P. Shum[‡]

Contribution from the Additives Analytical Research Department and Additives Research Department, Ciba Specialty Chemicals Corporation, 540 White Plains Road, P.O. Box 2005, Tarrytown, New York 10591, Physics, Novartis Services AG, Postfach, CH-4002, Basel, Switzerland, and Additives Research Department, Ciba Specialty Chemicals Corporation, P.O. Box 64, CH-1723 Marly 1, Switzerland

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Abstract: The conformation of the eight-membered membered 12H-dibenzo[d,g][1,3,2]dioxasilocin ring system was investigated both in the solid-state by X-ray crystallography and in solution by NOE experiments. *Ab initio* Hartree– Fock calculations were performed to locate all stationary points for the unsubstituted 12H-dibenzo[d,g][1,3,2]dioxasilocin ring system. The MM2* force field was parametrized to reproduce our *ab initio* results, and these data were compared to the experimental data. The transition states for conformational interchange were identified. The pseudoequatorial preference for a methyl substituent on either the C(12) carbon atom or silicon is greater than the difference in energy between a boat-chair and twist-boat conformation in 2,4,8,10-tetra-*tert*-butyl-substituted 12*H*dibenzo[*d*,*g*][1,3,2]dioxasilocins. The conformations observed in the solid-state X-ray crystal structures of 12*H*dibenzo[*d*,*g*][1,3,2]dioxasilocins are sensitive to crystal-packing forces and may be different from that in solution.

Introduction

Although numerous studies have appeared on the conformational dependence of both carbocyclic and small-membered heterocyclic compounds, the conformational analysis of mediumsized heterocycles has received little attention until quite recently.² First described in the pioneering work of Zuckerman^{3,4} in 1962, the eight-membered 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin ring system remained essentially unnoticed until our variable-temperature (VT) ¹H NMR studies in 1984.⁵ On the basis of the results of ¹H and ¹³C NMR spectral studies, we suggested the conformation of **1** was consistent with either a boat-chair (BC) or boat-boat (BB) conformation (both possessing C_S symmetry), although twist-boat (TB), boat (B), or twist (T) conformations that rapidly pass through the required symmetry plane could not be excluded (Figure 1).⁶

In a recent study, Arbusov *et al.* suggested a BC conformation for **2** in solution and dismissed consideration of the BB conformation based upon arguments that suggest a high groundstate energy for this conformation.⁷ In the related eightmembered 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring system, Arshinova advanced similar arguments against the BB conformation based upon MO calculations and a consideration of molecular models.^{6f,8,9} However, recent NMR spectral and crystallographic studies have shown evidence for the BB conformer in certain 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphos-

 $^{^\}dagger$ Additives Analytical Research Department, Ciba Specialty Chemicals Corp., New York.

[‡] Additives Research Department, Ciba Specialty Chemicals Corp., New York.

[§] Novartis Services AG.

^{II} Ciba Specialty Chemicals Corp., Switzerland.

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^{(2) (}a) Glass, R. S., Ed. Conformational Analysis of Medium-Sized Heterocycles; VCH: Weinheim, 1988. (b) Holmes, R. R.; Prakasha, T. K.; Pastor, S. D. In Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis; Quin, L. D., Verkade, J. G., Eds.; VCH: New York, 1994; pp 27–29. (c) Pastor, S. D. Trends Organomet. Chem. **1994**, *1*, 63.

^{(3) (}a) Zuckermann, J. J. J. Chem. Soc. **1962**, 873. (b) Zuckerman, J. J. J. Chem. Soc. **1963**, 1322. (c) Emeleus, H. J.; Zuckermann, J. J. J. Organomet. Chem. **1964**, 1, 328. (d) Silcox, C. M.; Zuckerman, J. J. J. Am. Chem. Soc. **1966**, 88, 168.

⁽⁴⁾ For related work, see: (a) Schwarz, R.; Kucken, W. Z. Anorg. Allg. Chem. 1955, 84, 279. (b) Von Ismail, R. M. Z. Anorg. Allg. Chem., Ser. B 1963, 18, 1124. (c) Von Ismail, R. M. Z. Naturforsch. B: Chem. Sci. 1964, 19, 873. (d) Allcock, H. R.; Nugent, T. A.; Smeltz, L. A. Synth. React. Inorg. Met.-Org. Chem. 1972, 2, 97. (e) Littlefield, L. B.; Doak, G. O. Phosphorus Sulfur 1977, 3, 35.

^{(5) (}a) Pastor, S. D.; Spivack, J. D.; Rodebaugh, R. K.; Bini, D. J. Org. Chem. **1984**, 49, 1297. (b) Pastor, S. D.; Spivack, J. D.; Steinhuebel, L. P. J. Heterocycl. Chem. **1984**, 21, 1285. (c) Pastor, S. D.; Denney, D. Z. Phosphorus Sulfur **1987**, 32, 105.

⁽⁶⁾ For discussions on the nomenclature of eight-membered rings, see:
(a) Hendrickson, J. B. J. Am. Chem. Soc. 1964, 86, 485. (b) Fraser, R. R.;
Raza, M. A.; Renaud, R. N.; Layton, R. B. Can. J. Chem. 1975, 53, 167.
(c) Anet, F. A. L.; Yavari, I. J. Am. Chem. Soc. 1977, 99, 6986. (d) Moore,
J. A.; Anet, F. A. L. In Comprehensive Heterocyclic Chemistry; Lwowski,
W., Ed.; Pergamon Press: Oxford, 1984; Vol. 7, pp 653-707. (e) Arshinova,
R. P.; Danilova, O. I.; Arbusov, B. A. Phosphorus, Sulfur, Silicon Relat.
Elem. 1987, 34, 1. (f) Arshinova, R. P. Russ. Chem. Rev. 1988, 57, 1142.
(7) Arbusov, B. A.; Klochkov, V. V.; Egorova, L. V.; Il'yasov, K. A.;

⁽r) Arbiasov, D. A., Rochikov, V. V., Egolova, L. V., Ir yasov, R. A., Arshinova, R. P. *Dokl. Akad. Nauk SSSR (Engl. Transl.)* **1989**, *305*, 80. (8) (a) Arshinova, R. P.; Plyamovatyi, A. Ch.; Kadyrov, R. A.;

<sup>Gnevashev, S. G.; Arbusov, B. A. Phosphorus, Sulfur, Silicon Relat. Elem.
1989, 41, 449. (b) Arshinova, R. P. Phosphorus, Sulfur, Silicon Relat. Elem.
1992, 68, 155.
(9) For the original suggestion of a BB conformation, see: Odorisio, P.</sup>

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Figure 1. The Chemical Abstracts numbering system and conformations of the 12H-dibenzo[d,g][1,3,2]dioxasilocin ring system. The TB conformation illustrated is one member of the family of flexible TB forms.

phocins.^{10–13} The BB conformation has been observed in the solid-state for certain 12*H*-dibenzo[d,g][1,3,2]dioxametallocins.^{14–16}

The unexpected diequatorial disposition of sterically hindered 12H-dibenzo[d,g][1,3,2]dioxaphosphocins in pentaoxyphosphoranes was reported by Holmes and co-workers, $1^{3,17-29}$ which

(10) Goddard, J. D.; Payne, A. W.; Cook, N.; Luss, H. R. J. Heterocycl. Chem. 1988, 25, 575.

(11) Rzepa, H. S.; Sheppard, R. N. J. Chem. Res. S 1988, 102.

(12) (a) Reddy, C. D.; Reddy, R. S.; Reddy, M. S.; Krishnaiah, M.; Berlin, K. D.; Sunthankar, P. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1991**, *62*, 1.
(b) Reddy, C. D.; Reddy, R. S.; Raju, C. N. *Asian J. Chem.* **1991**, *3*, 63. (c)
Reddy, C. D.; Reddy, R. S. N.; Raju, C. N.; ElMasri, M.; Berlin, K. D.;
Subramanian, S. *Magn. Reson. Chem.* **1991**, *29*, 1140. (d) Reddy, C. D.;
Berlin, K. D.; Reddy, R. S.; Raju, C. N.; Elmasri, M.; Subramanian, S. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1993**, *81*, 61. (e) Reddy, B. S.;
Reddy, C. D.; Reddy, P. M. *Heteroatom. Chem.* **1994**, *5*, 507. (f) For related work, see: Reddy, C. D.; Reddy, P. M.; Reddy, D. R.; Nagalakshmamma, M.; Anuradha, K.; Naga Raju, C.; Berlin, K. D.; Couch, K. M.; Tyagi, S. J. *Heterocycl. Chem.* **1995**, *32*, 1483. (g) Reddy, C. D.; Reddy, B. S.; Anuradha, K.; Berlin, K. D.; Naidu, S. M.; Krishnaiah, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3459.

(13) Prakasha, T. K.; Day, R. O.; Holmes, R. R. Inorg. Chem. 1992, 31, 3391.

(14) (a) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. Angew. Chem., Int. Ed. Engl. **1989**, 28, 66. (b) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. Inorg. Chem. **1991**, 30, 145.

(15) Toscano, P. J.; Schermerhorn, E. J.; Dettelbacher, C.; Macherone, C.; Zubieta, J. J. Chem. Soc., Chem. Commun. **1991**, 933.

(16) Okuda, J.; Fokken, S.; Kang, H.-C.; Massa, W. Chem. Ber. 1995, 128, 221.

(17) Swamy, K. C. K.; Sreelatha, C.; Day, R. O.; Holmes, J.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3126.

(18) Prakasha, T. K.; Day, R. O.; Holmes, R. R. Inorg. Chem. 1992, 31, 725.

(19) Hans, J.; Day, R. O.; Howe, L.; Holmes, R. R. Inorg. Chem. 1992, 31, 1279.

(20) Prakasha, T. K.; Day, R. O.; Holmes, R. R. Inorg. Chem. 1992, 31, 1913.

(21) Prakasha, T. K.; Day, R. O.; Holmes, R. R. Inorg. Chem. 1992, 31, 3391.

(22) Prakasha, T. K.; Burton, S. D.; Day, R. O.; Holmes, R. R. Inorg. Chem. 1992, 31, 5494.

(23) Holmes, R. R.; Prakasha, T. K.; Day, R. O. Inorg. Chem. 1993, 32, 4360.

(24) Prakasha, T. K.; Day, R. O.; Holmes, R. R. J. Am. Chem. Soc. 1993, 115, 2690.

(25) (a) Prakasha, T. K.; Day, R. O.; Holmes, R. R. Inorg. Chem. 1994,

33, 93. (b) Prakasha, T. K.; Day, R. O.; Holmes, R. R. Phosphorus, Sulfur, Silicon Relat. Elem. 1995, 100, 195. (c) Chandrasekaran, A.; Day, R. O.;

Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 2585. (d) See also: Wong, C. Y.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **1996**, *35*, 325.

(26) Holmes, R. R.; Dieters, J. A. Inorg. Chem. 1994, 33, 3235.

has important implications for the mechanism of nucleophilic substitution at tetracoordinate phosphorus.³⁰ These investigations led to the discovery of hypervalent phosphorus in sulfurcontaining eight-membered rings, e.g., $3.^{25,27}$ In the search of models for nucleophilic displacement reactions at silicon, sulfurinduced pentacoordination was observed in silanes incorporating sulfur-containing eight-membered rings, e.g., $4.^{31-33}$ Experi-



mental evidence was provided by Holmes et al. suggesting that electronic as well as steric effects induce coordination of the sulfur atom to silicon.³⁴ A series of organosilanes were prepared whose crystal structures showed geometries at silicon intermediate between tetrahedral and trigonal bipyramidal as a result of sulfur-induced coordination,³⁴ which provided useful models for studying the reactivity of silicon in nucleophilic displacement reactions.³⁵ Pentacoordinated organosilicon compounds are known to exhibit enhanced reactivity compared to tetracoordinated analogues.³⁵ Quite recently, we reported that the 12Hdibenzo[d,g][1,3,2]dioxasilocin **1** has a BB conformation in the solid-state.³⁶ Understanding the interesting conformational diversity as well as bonding properties of these sterically congested molecules requires a better understanding of the steric and electronic factors that dictate their stereochemistry. Indeed, investigations in the related sterically encumbered dibenzo[d.f]-[1,3,2]dioxaphosphepins and 12H-dibenzo[d,g][1,3,2]dioxaphosphocins have led to the development of new phosphite ligands for transition-metal-catalyzed reactions.³⁷

We report herein a solution NMR, crystallographic, and computational study to provide insights into the factors influencing the conformational behavior of the eight-membered 12H-dibenzo[d,g][1,3,2]dioxasilocin ring system. Additionally, the

(28) Prakasha, T. K.; Chandrasekaran, A.; Day, R. O; Holmes, R. R. Inorg. Chem. 1995, 34, 1243.

(29) For an early NMR spectral study that suggested diequatorial placement of an eight-membered ring, see: Abdou, W. M.; Denney, D. B.

Denney, D. Z.; Pastor, S. D. *Phosphorus Sulfur* 1985, 22, 99.
 (30) (a) Holmes, R. R. *Main Group Chem. News* 1993, 1, 18. (b) Holmes,

R. R.; Dieters, J. A. *Inorg. Chem.* **1994**, *33*, 3235. (31) Holmes, R. R.; Prakasha, T. K.; Srinivasan, S.; Day, R. O.

Phosphorus, Sulfur, Silicon Relat. Elem. 1994, 95–96, 375. (32) Holmes, R. R.; Prakasha, T. K.; Day, R. O. Phosphorus, Sulfur,

(32) Holmes, K. K., Hakasha, T. K., Day, K. O. Phosphorus, Suljur, Silicon Relat. Elem. **1994**, 87, 59.

(33) Day, R. O.; Prakasha, T. K.; Holmes, R. R. Organometallics 1994, 13, 1285.

(34) (a) Prakasha, T. K.; Srinivasan, S.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. J. Am. Chem. Soc. **1995**, 117, 10003. (b) Holmes, R. R. Chem. Rev. **1996**, 96, 927. (c) Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. Inorg. Chem. **1996**, 35, 3614. (d) For an interesting new development, see: Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. Inorg. Chem. **1996**, 35, 6552.

(35) (a) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17. (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

(36) Clark, F. H.; Fuhrer, H.; Meier, H.; Pastor, S. D.; Rist, G.; Shum, S. P. *Helv. Chim. Acta* **1993**, *76*, 1476.

⁽²⁷⁾ For an extensive discussion of stereochemistry and intermediates involving pentacoordinate phosphorus, see: (a) Luckenbach, R. Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements; G. Thieme: Stuttgart, 1973. (b) Holmes, R. R. Pentacoordinated Phosphorus: Reaction Mechansisms, Vol. I; ACS Monograph 176; American Chemical Society: Washington, DC, 1980. (c) Holmes, R. R. Pentacoordinated Phosphorus: Reaction Mechansisms, Vol. II; ACS Monograph 176; American Chemical Society: Washington, DC, 1980.

Table 1. Selected ¹H and ²⁹Si{¹H} NMR Spectral Shifts at -40 °C in CD₂Cl₂⁵⁷

compd	C(12)-H _{ax}	C(12)-H _{eq}	$^{2}J_{\mathrm{HCH}}$	SiMe _{ax}	SiMe _{eq}	SiH	Si ^e
1	4.20	3.43	-15.0	0.57	0.18		-6.8 ^f
2	4.18	3.38	-15.0	0.60	0.03		-4.8^{f}
7a _{MAJOR}	4.37	3.43	-13.1^{d}		0.72	4.57	-19.4
7a _{MINOR}	4.45	3.55	-15.4^{d}		0.65	5.75	а
7b _{TRANS}	4.92				0.67	4.47	-19.4
$7b_{CIS}$	4.61				0.57	5.75	-27.0
7c	4.69			0.58	0.08		-7.1
7d	3.85	3.70	-16.0	0.52	0.40		-4.2
7e	3.87	3.82	-16.0	0.50	0.37		-4.4
7f _{MAJOR}	3.92	3.83	-16.0		0.45	5.14	-18.8
7f _{MINOR}	3.98	3.93	-16.5	0.63		5.35	-18.3
$\mathbf{7g}^{b}$	4.28	3.42	-13.4			4.48; 5.07	С

^{*a*} Not observed. ^{*b*} Obtained at -95 °C in CD₂Cl₂. ^{*c*} Not measured. ^{*d*} Obtained at -69.5 °C in CD₂Cl₂. ^{*e*} Obtained at -40 °C in CDCl₃. ^{*f*} Obtained at -40 °C in CDcl₂.

computational work included empirical force field (MM2^{*}) parameterization *via ab initio* calculations to accurately model the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin ring system.³⁸ Early calculations on both the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin and 12*H*-dibenzo[*d*,*g*][1,3,2]-dioxaphosphocin ring systems were performed using nonempirical LCAO SCF calculations on small model compounds employing the STO-3G minimal basis set,^{7,39} which is known to be somewhat unreliable for second row elements.⁴⁰ We report herein calculations for the complete 12*H*dibenzo[*d*,*g*][1,3,2]dioxasilocin ring using a 6-31G^{**} splitvalence plus polarization basis set, which is particularly important for compounds including elements of the second row.⁴⁰

Results and Discussion

Synthesis of Model Compounds. The synthesis of dibenzo-[d,g][1,3,2]dioxasilocins by the reaction of a bisphenol with a dihalosilane derivative has been previously described.⁵ The 12*H*-dibenzo[d,g][1,3,2]dioxasilocins 1, 2, 7a-c, and 7g that were unsubstituted in the 1 and 11 ring positions were prepared using this standard methodology (see Table 1). For 7b, a mixture of cis and trans isomers was obtained from which the trans isomer 7b_{TRANS} could be isolated by flash chromatography.

Quite recently, Meier *et al.* described the synthesis of 1,11substituted 12*H*-dibenzo[d,g][1,3,2]dioxathiocins in which the steric interaction of these substituents precluded the BC or BB conformation.⁴¹ NMR spectroscopic and solid-state cyrstallographic studies of these 1,11-substituted 12*H*-dibenzo[d,g]-[1,3,2]-dioxathiocins indicated that a B conformation was obtained in both solution and the solid state. An analogous

(37) (a) Billig, E.; Abatjoglou, A. G.; Bryant, D. R. US Pat. 4,748,261, 1988; *Chem. Abstr.* **1987**, *107*, 7392. See also: (b) Babin, J. E.; Whiteker, G. T. US Pat. 5,360,938, 1994; *Chem. Abstr.* **1995**, *122*, 186609. (c) Buisman, G. J. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. Tetrahedron: Asymmetry **1993**, *4*, 1625. (d) van Leeuwen, P. W. N. M.; Buisman, G. J. H.; van Rooy, A.; Kamer, P. C. J. *Recl. Trav. Chim. Pays-Bas.* **1994**, *113*, 61. (e) See also: Jongsma, T.; Fossen, M.; Challa, G.; van Leeuwen, P. W. N. M. J. Molec. Catal. **1993**, *83*, 17. (f) van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; van Leeuwen P. W. N. M. Organometallics **1995**, *14*, 34. (g) Buisman, G. J. H.; Martin, M. E.; Vos, E. J.; Klootwijk, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1995**, *6*, 719.

(38) (a) Weiner, S. J.; Kollman, P. A.; Case, D. A.; Singh, U. C.; Ghio, C.; Alagona, G.; Profeta, S., Jr.; Weiner, P. J. Am. Chem. Soc. **1984**, 106, 765 and references therein. (b) Weiner, S. C.; Kollman, P.; Nguyen, D. T.; Case, D. A. J. Comput. Chem. **1986**, 7, 230. (c) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, T.; Still, W. C. J. Comput. Chem. **1990**, 11, 440.

(39) Arbusov, B. A.; Arshinova, R. P.; Danilova, O. I.; Kadirova, V. Kh.; Mukmeneva, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim (Engl. Transl.)* **1986**, 1601.

(40) (a) For a discussion of basis sets, see: Clark, T. A Handbook of Computational Chemistry; Wiley: New York, 1985; pp 233–242. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. P.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley: New York, 1986.

(41) Hug, P.; Meier, H.; Pitteloud, R.; Poppinger, D.; Rihs, G.; Rist, G. Helv. Chim. Acta 1990, 73, 618.



b. $R^{1}=t$ -Bu; $R^{2}=H$; $R^{3}=Re$; $R^{3}=H$; $R^{3}=Me$ c. $R^{1}=t$ -Bu; $R^{2}=H$; $R^{3}=R^{4}=R^{5}=Me$ d. $R^{1}=H$; $R^{2}=Me$; $R^{3}=H$; $R^{4}=R^{5}=Me$ e. $R^{1}=R^{2}=Me$; $R^{3}=H$; $R^{4}=R^{5}=Me$ f. $R^{1}=R^{2}=Me$; $R^{3}=R^{4}=H$; $R^{5}=Me$ g. $R^{1}=t$ -Bu; $R^{2}=R^{3}=R^{4}=R^{5}=H$

strategy was employed to prepare 12*H*-dibenzo[d,g][1,3,2]dioxasilocins that adopt a B conformation. The 1,11-substituted derivatives **7d**-**f** were prepared by the reaction of the appropriate dihalosilane with the corresponding bisphenol^{42,43} in the presence of triethylamine as a hydrogen chloride acceptor.

Solution and Solid-State Conformation. Previously, a VT ¹H NMR study on the dimethyl-substituted derivative 1 suggested that at room temperature rapid ring inversion of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin ring occurs.^{5a} The free energy of activation (ΔG^{\ddagger}) for ring inversion of 1 is 13.9 kcal/mol. Rapid ring inversion results in an averaging of the proton coupling constants of the various conformations present and prevents obtaining stereochemical information of the predominate conformer present.⁴⁴ This stereochemical averaging was mitigated by measuring appropriate coupling constants and NOEs below the coalescence temperature (*T*_C) for ring inversion.

⁽⁴²⁾ Casiraghi, G.; Casnati, G.; Pochini, A.; Ungaro, R.; Sartori, G. Synthesis 1981, 143.

⁽⁴³⁾ Summers, C. G.; Young, E. J. US Pat. 3632553; Chem. Abstr. 1972, 76, 128468.

⁽⁴⁴⁾ Eliel, E. L.; Wilen, S. H. Stereochemistry of Organic Compounds, 2nd ed.; Wiley: New York, 1994; pp 641-647.

Table 2. NOE Enhancements (%) of 1, 2, and 7a-g Measured at -40 °C in $CD_2Cl_2^{57}$

	trans	sannular		<i>t</i> -Bu _{C(4)/C(}	8)
compd	$H_{C(12)}-H_{Si}$	H _{C(12)} -SiCH ₃	SiHax	$CH_3Si_{ax} \\$	CH ₃ Si _{eq}
1		3		14	15
2		2		8	9
7a _{MAJOR}	0	0	24		11
7b _{trans}	0	0	23		13
7b _{CIS}	23	0	0		14
7c		4		13	17
7d		8		13	17
7e		4		11	8
7f _{MAJOR}	5	0	12		15

The ${}^{2}J_{\text{HCH}}$ coupling constant of the C(12)-geminal protons and NOEs reported for all of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin derivatives of this study were determined below the observed T_{C} at -40 °C (Tables 1 and 2).

The originally observed dependence for the geminal ${}^{2}J_{\rm HCH}$ coupling constant of the C(12)-geminal protons in substituted 5,6,7,12-tetrahydrodibenzo[a,d]cyclooctenes with ring conformation 45-48 was extended to probe the conformation of 12Hdibenzo[d,g][1,3,2]dioxaphosphocins in solution.^{6e,f,8a,b} The observation of a geminal coupling constant of -12 to -13 Hz in 12*H*-dibenzo[d,g][1,3,2]dioxaphosphocins is consistent with a BC (or BB) conformation with the exocyclic substituent on phosphorus assuming a pseudoequatorial placement, whereas TB and B conformations were associated with coupling constants ranging from -14 to -19 Hz.^{8b} Arbusov et al. further applied this probe to the 12H-dibenzo[d,g][1,3,2]dioxasilocin ring system.⁷ The magnitude of the geminal ${}^{2}J_{\rm HCH}$ coupling constant for the C(12)-geminal protons in 12H-dibenzo[d,g]-[1,3,2]dioxametallocins is dependent on the orientation of the C(12)-H bond relative to the π orbitals of the two aromatic rings. The hyperconjugative contribution to the magnitude of the geminal coupling reaches a minimum when the C(12)-H bonds are perpendicular to the π orbitals of the aromatic rings, as approached in the BC and BB conformation.46,47,48

In the ¹H NMR spectrum of **1** at -40 °C, two doublets are observed at δ 3.61 and 4.50 with ${}^{2}J_{\text{HCH}} = -15.0$ Hz, which are assigned to the two nonequivalent C(12)-methylene protons.⁴⁹ Two singlets were observed at 0.18 and δ 0.57, which were assigned to the protons of two nonequivalent methyl groups bonded to silicon. Both the VT 1H NMR and $^{13}C\{^1H\}$ NMR spectra of 1 below the $T_{\rm C}$ showed two equivalent pairs of *tert*butyl groups. All other atoms expected to be equivalent were observed to be so. Both the ¹H NMR and ¹³C{¹H} NMR spectral data of 1 below the $T_{\rm C}$ requires that the ring conformation possess a σ plane of symmetry passing through the silicon atom and the C(12) (bridging methylene) carbon atom such as found in the BB or BC conformation (C_S symmetry). This must be the case to explain both the observation of nonequivalent methyl groups bonded to silicon and nonequivalent C(12)methylene protons along with the observation of two equivalent pairs of *tert*-butyl groups below the $T_{\rm C}$. However, the magnitude of the observed ${}^{2}J_{HCH}$ geminal coupling constant (-15.0 Hz) for the C(12)-methylene protons below the T_C is inconsistent with either a BB or BC conformation. The observed ${}^{2}J_{\rm HCH}$ geminal coupling constant of -15.0 Hz is consistent with enantiomeric TB conformations (C_2 symmetry) that rapidly interconvert through structures possessing the required symmetry plane as either a transition state or intermediate. However, the participation of some population of either the BC or BB conformation in rapid equilibrium with the predominant population of TB conformations cannot be ruled out, *vide infra*. The BB conformer is the most likely intermediate or transition state for interconversion of enantiomeric TB conformations (TB \leftrightarrows TB*), *vide infra*.

Previously, we reported that the solid-state conformation of **1** is a BB. However, caution must be exercised in the comparison of conformations obtained from X-ray structural data with those in solution. Anet and Yavari warned that lattice energy and the resultant crystal-packing effects in the solid state can render the solid-state conformation different from that in solution.⁵⁰ For a range of pentacoordinated phosphorus compounds, Maciel *et al.* showed that the solid-state and solution conformations did not vary significantly.⁵¹ Similar conclusions were reached by Holmes and co-workers.^{20,52} However, *for the 12H-dibenzo[d,g][1,3,2]dioxasilocin derivatives of this study, the solid-state and solution conformations may be different*, which appears to be the case for **1** where the solution state conformation is predominantly a TB and the solid-state conformation is a BB.

To verify the difference between the solid-state and solution conformation of 1, NOE studies below the $T_{\rm C}$ of 1 were undertaken (see Table 2). A small transannular NOE was observed between one of the methyl groups bonded to silicon and one of the C(12)-methylene protons. The observation of a NOE enhancement between the (endocyclic) axial C(12)methylene proton and the (endocyclic) axial methyl group protons bonded to silicon of 1 is consistent with a BB conformation. However, the observed NOE is an average of the ensemble of conformations present in solution.⁵³ Although this averaging is often considered unimportant and an average solution structure is referred to, Torda and van Gunsteren warn that this viewpoint can be totally inappropriate.⁵³ Indeed, the observed NOE for a rapid equilibration of TB structures that pass through the BB form as either a transition state or intermediate will reflect a contribution of the BB conformation. The observed NOE will be a time-averaged population of all conformations present in solution. Indeed, the magnitude of the observed NOE between the axial methylene proton and the protons of one methyl group bonded to silicon, the ${}^{2}J_{\rm HCH}$ geminal coupling constant, and calculations (vide infra) strongly suggest that 1 exists predominantly as a TB conformation in solution. The observation of a nearly equal NOE between both methyl group protons bonded to silicon and the protons of the C(4) and C(8) tert-butyl groups is further evidence for a TB conformer. This is the case because, in a BB conformation, the endocyclic methyl group protons would not be expected to exhibit a NOE to either of the C(4) and C(8) tert-butyl groups. A clear caveat to conclusions regarding the conformation of eight-membered 12H-dibenzo[d,g][1,3,2]dioxasilocin ring system is that the solid state and solution conformations may be different.

The conformational study of 1 led us to reinvestigate the solution conformation of 2, which was previously reported by

⁽⁴⁵⁾ Renaud, R. N.; Bovenkamp, J. W.; Fraser, R. R.; Roustan, J.-L. A. Can. J. Chem. 1977, 55, 3456.

⁽⁴⁶⁾ Barfield, M.; Grant, D. M. J. Am. Chem. Soc. 1963, 85, 1899.

⁽⁴⁷⁾ Pople, J. A.; Bothner-By, A. A. J. Chem. Phys. **1965**, 42, 1339.

^{(48) (}a) Barfield, M.; Sternhell, S. J. Am. Chem. Soc. 1972, 94, 1905.
(b) Barfield, M.; Grant, D. M. J. Am. Chem. Soc. 1964, 83, 4726.

⁽⁴⁹⁾ The two-bond geminal coupling constant is presumed to be negative. See: Jackman, L. S.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: Oxford, U.K., 1969; pp 270–279.

⁽⁵⁰⁾ Anet, F. A. L.; Yavari, I. J. Am. Chem. Soc. 1977, 99, 6986.

⁽⁵¹⁾ Dennis, L. W.; Bartuska, V. J.; Maciel, G. E. J. Am. Chem. Soc. **1982**, 104, 230.

⁽⁵²⁾ Holmes, R. R.; Prakasha, T. K. Phosphorus, Sulfur, Silicon Relat. Elem. 1993, 80, 1.

^{(53) (}a) Torda, A. E.; van Gunsteren, W. F. In *Reviews in Computational Chemistry III*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: Weinhein, 1992; pp 153–155. (b) For a recent account, see: Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: Weinheim, 1989.

Table 3. Solid-State and Solution Conformation of 1, 2, and 7a-g along with Selected Stereochemical Indicators⁵⁷

	confe	ormation		Δά	8	NOE e	nhancements
compd	solid	solution	$^{2}J_{\mathrm{HCH}}$	C(12)H ₂	SiMe ₂	HC(12)-H _{Si}	t-Bu _{C(4)/C(8)} -SiH _{ax}
1 ³⁶	BB	TB	-15.0	0.77	0.39		
2		TB	-15.0	0.80	0.57		
7a _{MAJOR}	BC	BC	-13.1°	0.94		0	24
7a _{MINOR}		TB	-15.4°	0.90		а	а
7b _{TRANS}	BC	BC				0	23
7b _{CIS}		TB				23	0
7c	BC	TB			0.50		b
7d	В	В	-16.0	0.15	0.12		
7e		В	-16.0	0.05	0.13		
7f _{MAJOR}		В	-16.0	0.09		5	12
7f _{MINOR}		В	-16.5	0.05		а	а
$\mathbf{7g}^d$		BC	-13.4	0.86		а	а

^{*a*} Not determined. ^{*b*} Evidence for TB rather than BC conformation in solution provided by the observation of a NOE enhancement between the C(12) proton and the SiMe protons in **7c** and not in either **7a_{MAJOR}** or **7b_{TRANS}**. ^{*c*} Obtained at -69.5 °C in CD₂Cl₂. ^{*d*} Obtained at -95 °C.

Arbuzov et al. to possess a BC conformation in solution. A $^{2}J_{\text{HCH}}$ geminal coupling constant of -13.8 Hz for 2 was reported in a mixed solvent system of carbon disulfide and dichloromethane- d_2 .⁷ The observed NOE and ²J_{HCH} geminal coupling constant of **2** in dichloromethane- d_2 (Tables 2 and 3) are consistent with a TB conformation in solution. Observed coupling constants are weighted averages of conformational contributors,⁴⁴ and the reported differences in the ${}^{2}J_{\text{HCH}}$ geminal coupling constants may reflect a difference in the population of the family of TB conformations present due to a change in the solvent medium.⁵⁴ For certain solvents such as dichloromethane- d_2 , significant changes in dielectric constant with temperature⁵⁵ can lead to changes in conformer distribution, which warns against comparisons using tools such as ${}^{2}J_{\rm HCH}$ without appropriate precautions to insure a valid comparison. A particular dramatic effect of temperature was demonstrated by Denney and Pastor on the structural dependence of a pentaoxyphosphorane in dichloromethane- d_2 .⁵⁶ A TB conformation for 2 in solution is also supported by the similarity of the difference in chemical shifts between the protons attached to the C(12) carbon atom ($\Delta \delta = 0.77$ and 0.80, respectively) and methyl group protons bonded to silicon ($\Delta \delta = 0.39$ and 0.57, respectively) in the ¹H NMR spectra of 1 and 2 (see Table 3).

An X-ray crystal structure of **7a** was obtained to determine the effect of one less methyl group bonded to silicon on the conformational preference. A BC conformation in the solid state is observed for **7a** (see Figures 2 and 3). The methyl group bonded to silicon assumes a pseudoequatorial position in the eight-membered ring, whereas the hydrogen bonded to silicon assumes a pseudoaxial position.⁵⁷ The proton bonded to silicon is located in a cleft between the 4- and 8-*tert*-butyl substituents. These observations suggests that the expected BC conforma-

(57) In the BC conformation, substituents on silicon and the C(12)methylene carbon atom of the silocin ring will be refered to as pseudoequatorial and pseudoaxial analogous to the nomenclature of cyclohexane. For clarity in the TB family of conformations, substituents on silicon and the C(12)-methylene carbon atom of the silocin ring will be refered to as either endo- (pointing toward the inside of the boat-like concave ring system) or exocyclic (pointing to the outside of the ring). The endocyclic substituents would correspond to a pseudoaxial position, whereas an exocyclic substituent would correspond to a pseudoaxial position.

(58) (a) In eight-membered 12H-dibenzo[d,g][1,3,2]dioxametallocins rings, the BC conformation is generally expected to be lowest in energy. For discussions see: ref 2a and references therein. (b) For a discussion in carbocyclic systems, see: Zschunke, A. *Molekuelstruktur*; Spectrum Academic Press: Heidelberg, 1993; pp 130–131.



Figure 2. Pseudoaxial and pseudoequatorial positions in the BC conformation, and endocyclic and exocyclic positions in the family of TB conformations.



Figure 3. ORTEP of 7a_{MAJOR}.

tion⁵⁸ is obtained for **7a** because steric interactions between the proton bonded to silicon and the adjacent *tert*-butyl substituents are small. The lack of predominance of the BC conformation in both **1** and **2** can be explained in terms of a ground state destabilization of the BC conformer due to steric interactions between the methyl groups bonded to silicon and the adjacent

⁽⁵⁴⁾ Reference 44, p 700.

^{(55) (}a) For the dependence of solvent dielectric constant on temperature, see: Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955; pp 204–205. (b) For the temperature dependence of the dielectric constant of dichloromethane- d_2 , see: *Handbook of Chemistry and Physics*, 53rd ed.; CRC Press: Cleveland, OH, 1977; p E44.

⁽⁵⁶⁾ Denney, D. B.; Pastor, S. D. Phosphorus Sulfur 1983, 16, 239.

tert-butyl substituents. These steric interactions can be relieved in both **1** and **2** by a change in conformational preference from the BC to the TB family of conformations. These conclusions are supported by the observation that the solid-state conformations of analogous P(III)-containing 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocins are BC with the sterically undemanding lone pair of electron on phosphorus occupying a pseudoaxial position in the cleft between the 4- and 8-*tert*-butyl substituents.^{59,60,61}

In the ¹H NMR spectrum of **7a** at 120 °C ($C_2D_2Cl_4$), two doublets were observed at δ 3.59 and 4.21 that were assigned to two nonequivalent C(12)-methylene protons. In the ¹H NMR spectrum of **7a** below 10.5 °C (CD₂Cl₂), the $T_{\rm C}$, two pairs of nonequivalent C(12)-methylene protons as well as the protons of two nonequivalent methyl groups bonded to silicon were observed at unequal intensity. A reasonable explanation for this observation is that below the $T_{\rm C}$ two conformers of unequal population are being observed. A 95:5 ratio of conformers was measured at -70 °C by integration of the peak areas in the ¹H NMR spectrum of **7a**, which corresponds to a $\Delta G^{\circ}_{203} = 1.17$ kcal/mol. The free energies of activation (ΔG^{\dagger} required to render these diastereomeric conformers equivalent, calculated by the method of Shanan-Atidi and Bar-Eli for unequal populations of exchanging species,62 are 13.0 and 14.7 kcal/ mol.

In the ¹H NMR spectrum of major isomer 7a_{MAJOR} observed below $T_{\rm C}$, the C(12)-methylene protons are observed as two doublets at δ 3.38 and 4.31 with a ${}^{2}J_{\text{HCH}}$ geminal coupling constant of -13.1 Hz. The magnitude of the observed geminal coupling constant is consistent with a BC conformation for $7a_{MAJOR}$. The protons of the methyl group bonded to silicon were observed as a singlet at δ 0.67. No transannular NOEs were observed between the axial C(12)-methylene proton and either the proton or methyl group bonded to silicon. A strong NOE (24%) was observed between the proton bonded to silicon and the 4,8-tert-butyl substituent protons, which is expected to be the case when the proton is pseudoaxial in the cleft between the tert-butyl substituents in the BC conformation. Consistent with this interpretation, a moderate NOE (11%) is observed between the pseudoequatorial methyl group protons and the 4,8tert-butyl substituent protons. These results strongly suggest that in this case the solid state conformation is the same as the major conformational isomer in solution.

In the ¹H NMR spectrum of the minor isomer $7a_{MINOR}$ observed below $T_{\rm C}$, the C(12)-methylene protons are observed as two doublets at δ 3.53 and 4.37 with a ²J_{HCH} geminal coupling constant of -15.4 Hz. The magnitude of the observed geminal coupling constant is consistent with a TB conformation for 7a_{MINOR}. The protons of the methyl group bonded to silicon were observed as a singlet at δ 0.59. NOE studies were not carried out on 7a_{MINOR} because the low concentration present made such studies impractical. The reason that 7a_{MINOR} exhibits a TB conformation rather than a BC may be understood from the developing steric argument. Ring inversion of $7a_{MAJOR}$ would place the methyl substituent bonded to silicon in a pseudoaxial aptitude between the 4,8-tert-butyl substituents in a BC conformation with resultant ground state destabilization due to steric interactions as in 1 and 2, vide ante. To alleviate the resultant steric interactions that would exist in a BC



Figure 4. ORTEP of 7b_{TRANS}.

conformer, $7a_{MINOR}$ assumes a TB conformation with the methyl substituent on silicon assuming a exocyclic position.

In the solid-state X-ray crystal structure of $7b_{TRANS}$, a BC conformation is observed with both the C(12)-methyl substituent and the methyl group bonded to silicon assuming pseudoequatorial ring positions (Figure 4). In the solid-state conformation observed for $7b_{TRANS}$, the proton bonded to silicon is pseudo-axially placed between the cleft formed by the 4- and 8-*tert*-butyl substituents, which is what is expected on the basis of steric arguments. The solid-state X-ray structure of $7b_{TRANS}$ provides the first demonstration of trans conformational isomerism in a 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin. NOE studies support a similar BC conformation for $7b_{TRANS}$ in solution, particularly the observation of a strong NOE between the proton bonded to silicon and the 4,8-*tert*-butyl substituents (23%) and the absence of a transanular NOE between the C(12)-methylene proton and the proton bonded to silicon.

The cis isomer $7b_{CIS}$ could not be isolated free of the trans isomer. However, NOE studies in solution showed the absence of a NOE enhancement between the proton bonded to silicon and the 4,8-tert-butyl substituents and a strong transanular NOE enhancement between the C(12)-methylene proton and the proton bonded to silicon (23%). The results of the NOE study suggest a predominant TB conformation for 7b_{CIS} with the C(12)-methyl and Si-methyl substituents exocyclically (pseudoequatorially) placed. The TB structure of 7b_{CIS} with exocyclic placement of the methyl ring substituents avoids steric interactions due to endocyclic (pseudoaxial) placement of either the C(12)-methyl or Si-methyl substituent. This result strongly suggests that in the BC conformation, the exocyclic (pseudoequatorial) preference for a methyl substituent on either the C(12) carbon or silicon is larger than the difference in energy between a BC and TB in the 2,4,8,10-tetra-tert-butyl-substituted 12H-dibenzo[d,g][1,3,2]-dioxasilocin ring system. A similar finding was made by Arshinova in the 12H-dibenzo[d,g][1,3,2]dioxaphosphocin ring system.63

Contrary to expectations, a BC conformation was found for the 6,6,12-trimethyl-substituted derivative **7c** in the X-ray crystal structure determination (Figure 5). The C(12)-methyl substituent did assume the expected pseudoequatorial orientation. Quite interestingly, two independent molecules with closely related BC conformations were found in the unit cell that could not be transformed into one another by either a symmetry or translational operation. The crystal parameters for both molecules are listed in the Supporting Information. The difference between the two BC conformations **7c(I)** and **7c(II)** is seen in the torsional angles (see Table 4 in the Supporting Information). The Si–O bond lengths in **7c(I)** [Si(6)–O(7) = 1.63 Å and

⁽⁵⁹⁾ Pastor, S. D.; Shum, S. P.; DeBellis, A. D.; Burke, L. P.; Rodebaugh, R. K.; Clarke, F. H.; Rihs, G. *Inorg. Chem.* **1996**, *35*, 949.

⁽⁶⁰⁾ Pastor, S. D.; Rogers, J. S.; NabiRahni, M. A. Inorg. Chem. 1996, 35, 2157.

⁽⁶¹⁾ Litvinov, I. A.; Struchkov, Y. T.; Arbuzov, B. A.; Arshinova, R. P.; Ovodova, O. V. Zh. Strukt. Khim. **1984**, 25, 1118; Zh. Strukt. Khim. [Engl. Transl.] **1984**, 25, 943.

⁽⁶²⁾ Shanan-Atidi, H.; Bar-Eli, K. H. J. Phys. Chem. **1970**, 74, 961. A small error is introduced due to the neglect of coupling for the observed protons.

⁽⁶³⁾ Arshinova, R. P.; Danilova, O. I.; Ovodova, O. V. Dokl. Akad. Nauk SSSR **1986**, 287, 1135; Dokl. Akad. Nauk SSSR [Engl. Tranl.] **1986**, 287, 99.



Figure 5. ORTEP of 7c.

Si(6)-O(5) = 1.65 Å] and 7c(II) [Si(46)-O(45) = 1.65 Å and Si(46)-O(47) = 1.64 Å] are essentially identical and in the range expected for an Si-O bond (1.65 Å).⁶⁴ Similarly, the O-Si-O and Si-O-C bond angles in both 7c(I) and 7c(II) are essentially the same. There are no significant differences in bonding parameters between the two conformer molecules 7c(I) and 7c(II). The differences in conformation between 7c-(I) and 7c(II), as seen in the torsional angles, support the contention that crystal-packing forces in the solid state can have a strong influence on the observed conformation of the 12Hdibenzo[d,g][1,3,2]dioxasilocin ring system.

Indeed, NOE studies support a predominant TB conformation for 7c in solution. In particular, a small NOE enhancement is observed between the axial (or endocyclic) C(12) proton and the methyl group protons bonded to silicon that are similar in magnitude to that observed for 1 and 2. No enhancement would be expected between the C(12) proton and the methyl group protons bonded to silicon if 7c existed predominantly in a BC conformation as is the case for 7a_{MAJOR} or 7b_{TRANS}. NOE enhancements are observed for the protons of both methyl groups bonded to silicon and the 4,8-di-tert-butyl substituents that are also similar in magnitude to that observed for 1 and 2. These enhancements can be explained if 7c exists predominantly as a TB conformation in solution with the C(12)-methyl substituent pseudoequatorial. A TB conformation for 7c is further supported by the fact that the observed $\Delta\delta$ between the signals for the two methyl groups bonded to silicon is similar to that observed for 1 and 2.

The strategy of Meier et al.41 was employed to obtain an appropriate model for measuring spectral parameters of a 12Hdibenzo[d,g][1,3,2]dioxasilocin that would exist in the B conformation in solution. 1,11-Dimethyl substitution in a 12Hdibenzo[d,g][1,3,2]dioxasilocin forces the ring system into a B conformation in order to avoid steric interactions between the two methyl substituents in either the BC or BB conformation, vide infra. The ¹H NMR of the 1,11-dimethyl-substituted derivation 7d was consistent with these expectations. In the ¹H NMR of **7d** below the $T_{\rm C}$, two doublets were observed at δ 3.85 and 3.70, which were assigned to the two nonequivalent C(12) protons with ${}^{2}J_{\rm HCH} = -16$ Hz. The magnitude of the observed ${}^{2}J_{\text{HCH}}$ geminal coupling constant is consistent with a predominant B conformation in solution. This must be the case because the large absolute value of ${}^{2}J_{\text{HCH}}$ suggests that on a time average the major population of conformations present is near the B geometry that allows the maximum hyperconjugative contribution of the π orbitals to the geminal coupling constant, vide ante. Particularly interesting, the chemical shift difference



Figure 6. ORTEP of 7d.

 $(\Delta \delta)$ between the C(12)-methylene protons is small ($\Delta \delta = 0.15$ ppm) compared to that of the TB and BC conformers ($\Delta \delta = 0.77-0.94$ ppm). A similar difference was seen between the chemical shift difference of the anisochronous methyl groups bonded to silicon in the B versus the TB and BC conformations. An examination of Dreiding molecular models suggests that this is the case because in the B conformation both C(12) protons are in a similar environment with respect to the anisotropy effect of the aromatic rings (the B conformer is approaching the C_2 symmetric T conformation). The *magnitude* of the $\Delta \delta$ between the C(12)-methylene protons may provide an additional tool for differentiating between B and TB conformations in solution. The NOE experiments were consistent with a B conformer.

In the solid-state X-ray crystal structure of **7d**, a B conformation is observed (Figure 6). Characteristic for a B conformation, the O(5)–Si(6)–O(7)–C(15) torsion angle is near 0°, whereas the O(7)–Si(6)–O(5)–C(14) torsion angle is near 90–100° (-3° and -95° , respectively). The O(5)–Si(6)–O(7)–C(15) atoms lie in a plane. Anet noted that the B conformation lying halfway between a symmetric C_2 twist conformation and a BB conformation.^{6c} The Si–O bond lengths in **7d** [Si(6)–O(7) = 1.65 Å and Si(6)–O(5) = 1.64 Å] are in the range expected for a Si–O bond (1.65 Å).⁶⁴ The O(5)–Si(6)–O(7) bond angle of 108.0° in **7d** is smaller compared to the analogous O–Si–O bond angles in **1**, **7a_{MAJOR}**, **7b_{TRANS}**, and **7c** (111.0°, 115.8°, 113.1°, and 111.0°, receptively).

The 1,2,10,11-tetramethyl-substituted derivative **7e** would be expected to adopt a B conformation in solution. Consistent with this expectation, a ${}^{2}J_{\rm HCH}$ geminal coupling constant of -16 Hz is observed for the anisochronous C(12)-methylene protons of **7e**. Furthermore, the $\Delta\delta$ between the C(12)-methylene protons was small (0.05 ppm), *vide ante*.

In the ¹H NMR of the monomethyl-substituted silicon derivative **7f** below the $T_{\rm C}$, two pairs of anisochronous C(12)methylene protons are observed. In the major isomer of **7f**, a ²J_{HCH} geminal coupling constant of -16.0 Hz is observed for the C(12)-methylene protons with a $\Delta\delta$ of 0.09 ppm. The observation of a NOE enhancement between the protons on C(12) and Si, as well as between the methyl group protons bonded to silicon and the 4,8-di-*tert*-butyl protons, suggests a B conformation with the methyl group bonded to silicon exocyclic to the ring. In the ¹H NMR of the minor isomer of **7f**, a ²J_{HCH} geminal coupling constant of -16.5 Hz is observed for the C(12)-methylene protons with a $\Delta\delta$ of 0.05 ppm that suggests the minor isomer attains a B conformation with the methyl group bonded to silicon with the methyl group bonded to silicon with the methyl explanation with the methyl scale of 0.05 ppm that suggests the minor isomer attains a B conformation with the methyl group bonded to silicon with the methyl g

The dihydrido-substituted silicon derivative **7g** would be expected to exist as a BC in solution. This would be the case because of the lack of substitution on both C(12) and Si as well as the 1,11 positions on the aromatic rings. The observation of a ${}^{2}J_{\text{HCH}}$ geminal coupling constant of -13.4 Hz for the

⁽⁶⁴⁾ Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, D. G.; Taylor, R. J. Chem. Soc., Perkin Trans. 2 1987, S1.

⁽⁶⁵⁾ The torsion angles in the X-ray crystal structure of **7d** are negative because the enantiomeric conformation was observed.



Figure 7. Three-dimensional representations of the stationary points of the unsubstituted dioxasilocin ring system. Hydrogens have been omitted for clarity.



Figure 9. Ring-opened substructures used in parameterization.

anisochronous C(12)-methylene protons with a $\Delta\delta$ of 0.86 ppm is consistent with a BC conformation for **7g** in solution. Interestingly, in the ¹H NMR of **7g** below the *T*_C, the geminal ²*J*_{HCH} coupling constant of the nonequivalent protons bonded to silicon was 27.2 Hz (sign undetermined).

Computational Results

Ab Initio Calculations. Ab initio Hartree-Fock calculations were performed to locate all stationary points for the unsubstituted 12H-dibenzo[d,g][1,3,2]dioxasilocin ring system. The starting geometries for the calculations were taken from the structures of the corresponding stationary points of the analogous carbocycle6c,66 or from our previously reported semiempirical PM3⁶⁷ results.¹ Figures 7 and 8 (see the Supporting Information) show the geometrical results for the central ring obtained with the 6-31G* basis set. In general, the comparison with our experimental crystal structure of the substituted ring system is very good. Bond lengths are generally reproduced to within 0.01 Å, bond angles to about 4°, and dihedral angles to about 6°. Frequency analysis with both the STO-3G and 3-21G basis sets indicates that only the BC and TB conformers are stable minima, the others being transition states with a single imaginary frequency. Table 5 lists the absolute and relative energies of each stationary point for a number of basis sets. Both the geometry and energy were determined for each basis with the exception of the energies obtained with the larger 6-31G(2d,p) basis set for which a 6-31G** geometry was used. Zero-point or thermal energy corrections have not been applied to the energies.

Use of the 3-21G(*) basis resulted in the location of only three stationary points which have been characterized as one minimum (BC) and two saddle points. All attempts at minimizing to a TB resulted in convergence to the BC. The failure of this basis to reproduce the stable TB minimum may be due to an imbalance caused by the placement of polarization functions

Fable 5. A	b Initio Energies o	of Stationary P	oints of Unsubstitu	ted Dioxasiloc	cin Ring System U	sing Different	Basis Sets					
stationary point	STO-3G E (hartree)	E (rel) (kcal/mol)	3-21G E (hartree)	<i>E</i> (rel) (kcal/mol)	3-21G(*) E (hartree)	<i>E</i> (rel) (kcal/mol)	$6-31G^*$ <i>E</i> (hartree)	E (rel) (kcal/mol)	6-31G** <i>E</i> (hartree)	<i>E</i> (rel) (kcal/mol)	6-31G(2d,p) E (hartree)	<i>E</i> (rel) (kcal/mol)
BC	-926.602348 -926.598495	0.00 2.42	-932.897879 -932.896730	0.00 0.72	-933.018 500	0.00	-938.010741 -938.007222	0.00 2.21	$-938.031\ 212$ $-938.027\ 696$	0.00	$-938.056\ 135$ $-938.052\ 488$	0.00 2.29
BB (TS1) TS2	-926.588970 -926.587889	8.39 9.07	$-932.896\ 644$ $-932.896\ 682$	$0.77 \\ 0.75$	-933.017420	0.68	-938.004084 -938.005872	4.18 3.06	-938.024527 -938.026314	4.19 3.07	$-938.049\ 039$ $-938.050\ 929$	4.45 3.27
T (TS3)	-926.588 824	8.49	-932.872 935	15.65	-932.994 489	15.07	-937.994 605	10.13	-938.015 106	10.11	$-938.040\ 888$	9.57

^{(66) (}a) Allinger, N. L.; Viskocil, J. F., Jr.; Burkert, U.; Yuh, Y. *Tetrahedron* **1976**, *32*, 33. (b) Elhadi, F. E.; Ollis,W. D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1976**, *15* (4), 224.

^{(67) (}a) Stewart, J. J. P. J. Comput. Chem. **1989**, 10, 209. (b) Stewart, J. J. P. J. Comput. Chem. **1989**, 10, 221.

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only on the silicon atom. Removal of the polarization functions by using the 3-21G basis reestablishes the TB minimum, albeit with a distorted geometry (see the Supporting Information). Also, the energies obtained with any form of the 3-21G basis are very different from the results with the other basis sets. This is partially due to the distorted geometry of the TB. Finally, the addition of polarization functions on oxygen and carbon (6-31G* basis) also restores the TB minimum, and a further increase in the size of the basis set displays a reasonable convergence in the relative energies.⁶⁸

The relative energetic results of the calculations allow some observations to be made. The energetic penalty for interconversion of the enantiomeric TB forms through the BB (TS1), as well as the barrier for BC to TB interconversion (through TS2) being somewhat low. Conversely, ring inversion through the T (TS3) form occurs at a greater energetic cost. This is in agreement with the observed conformational flexibility of these systems and with the experimental result which associates the $T_{\rm C}$ observed with the ring inversion process.^{5a} The relative energies of the transition states can be understood in terms of the valence bond angles seen in each form. The majority of the ring strain in the BB (TS1) and TS2 structures arises from the valence angles about the oxygen atoms. The opening of the bond angles about oxygen in each structure is a relatively easy process.⁶⁹ Therefore, the two transition states are low in energy. On the other hand, most of the ring strain present in the T (TS3) structure is due to the wide valence angle about the C(12)-bridging-methylene carbon. The opening of this bond angle to 128° is a more difficult process, thereby raising the energy of this transition state.

An additional observation concerns the relative energy of the BB (TS1) conformation given by the minimal STO-3G basis set which was employed in previous work.⁷ The energy is close to that of the T (TS3) form and 4 kcal/mol greater than that given by the larger basis sets. As previously mentioned, the argument against this form was based on the supposed high ground-state energy of the BB.

Force Field Parametrization. An ab initio study of the effect of dimethyl substitution on silicon and 4,8 di-tert-butyl substitution on the conformational energetics of the present ring system would be very computationally demanding. As a result, we chose to parametrize the MM2* force field to reproduce our ab initio results. The resulting modified force field could then be used to study the effects of substitution. Four dihedral angles (C-C-O-Si, C-O-Si-H, C-O-Si-C, and C-O-Si-O), as well as one valence bond angle (C-O-Si), were parametrized. The unmodified force field indicated that the original dihedral parameters were of low quality, and the angle bending parameter was of medium quality.⁷⁰ Torsional parameters were developed by fitting to the HF/6-31G*//HF/6-31G* rotational profiles for the corresponding ring-opened substructures 8-10. Partial atomic charges were assigned from a fit to the molecular electrostatic potential of the HF/6-31G* wave function taken initially from the HF/6-31G* geometries of the ring-opened substructures and then adjusted to more closely match the charges from the heterocycle in the BC conformation. The angle-bending parameter about the oxygen atom was determined in a similar manner from calculations on structure 8. Lone pairs were not used in any structure and consequently

Table 6. MM2* Parameters Used in This Work

stretch	ı	r_0		k _r	diı	oole
Si-H		1.489	2	.720	1	.177
O-Si		1.650	5	.500	-2	.357
C-O		1.355	6	.000	1	.562
C4,8-H		1.101	4	.600	-0	.870
С1,11-Н		1.101	4	.600	-0	.580
С2,10-Н		1.101 4.600		-0.724		
С3,9-Н		1.101	1 4.600		-0	.580
C4a,7a-C4	,8	1.390	8.067		0	.801
C4a,7a-C1	2a,11a	1.390	8.067		0	.801
C11a,12a-0	211,1	1.390	8	.067	-0	.264
C4,8-C3,9		1.390	8	.067	-0	.264
C1,11-C2,	10	1.390	8	.067	0	.334
C3,9-C2,10)	1.390	8	.067	0	.334
bend		$ heta_0$	$k_{ heta}$		k _{str} -	bend
C–O–Si		135.0	0.35	0	0.0)0
torsion	V_1	V_2	V_3	V_4	V_5	V_6
C-O-Si-H	0.00	0.00	0.250	0.00	0.00	0.00
C-O-Si-O	-0.227	-0.850	0.1614	0.00	0.00	0.00
C-O-Si-C	0.601	-0.004	0.329	0.00	0.00	0.00
C-C-O-Si	0.00	0.797	0.00	0.044	0.00	0.011

 Table 7.
 Relative Energies of Stationary Points of the

 Dioxasilocin Ring System Calculated by a HF/6-31G* Calculations

 and with the MM2* Force Field

	unsubs	stituted	6,6-dimethyl- 4,8-di- <i>tert</i> -butyl substituted
stationary point	E (kcal/mol) MM2*	E (kcal/mol) ab initio	E (kcal/mol) MM2*
BC	0.0	0.0	0.0
BB (TS1)	3.8	4.2	2.5
TS2 T (TS3)	4.2 8.8	3.0 10.1	3.1 14.9

were not parametrized. The initially determined parameters for the ring-opened compounds were then used in molecular mechanics optimizations of the unsubstituted ring system. Unfortunately, the important BC–TB energy difference was calculated to be 2.6 kcal/mol, slightly greater than the 2.2 kcal/ mol *ab initio* determination. As a result, the V_2 parameter for the C–O–Si–O torsion was adjusted to –0.850 from the initial value of –1.346. The resulting parameters are listed in Table 6. Table 7 compares the relative energies of all stationary points of the unsubstituted ring system using the MM2* force field and the 6-31G* basis set.

Molecular Mechanics Calculations. As previously mentioned, the presently determined molecular mechanics parameters have been used to study the effects of dimethyl substitution on silicon and 4,8 di-tert-butyl substitution on the benzo rings. Table 7 lists the relative energies of the stationary points of the silicon and 4,8-substituted dioxasilocin ring system calculated with MM2*. A comparison with the energies of the unsubstituted structures indicates that substitution destabilizes the BC by 1.2 kcal/mol relative to the TB such that the two conformers are within 0.8 kcal/mol of one another. As there are twice as many TB conformers relative to BC, the addition of an entropy of mixing term (ca. 0.5 kcal/mol at -40 °C) decreases the difference to 0.3 kcal/mol. Therefore, the calculation suggests that there will be a significant population of the TB resulting from substitution. The experimental result shows that the predominant conformation at -40 °C in CD₂Cl₂ solution is the TB. The calculation therefore underestimates the degree of destabilization of the BC due to substitution, even though the predicted trend is in the correct direction. There may be several reasons for this apparently incorrect result. The force field calculations may underestimate the steric repulsion caused by

⁽⁶⁸⁾ A more complete analysis should include calculations to assess the contribution of electron correlation to the conformational energies, at least at the MP2 level. Unfortunately, given the size of the present system, the computer resources to perform such calculations were simply not available to us.

⁽⁶⁹⁾ Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schriber, S. L. J. Am. Chem. Soc. **1990**, 112 (2), 697.

⁽⁷⁰⁾ Introduction to Molecular Modeling with Macromodel; Department of Chemistry, Columbia University, New York, NY 10027.

silicon and 4,8-substitution and/or the *ab initio* calculations may have overestimated the energy difference between the BC and TB. Moreover, there may be additional entropic terms that we have not accounted for which favor population of the TB. Indeed, when the STO-3G vibrational frequencies are used (which probably underestimate the entropy of the TB as the STO-3G barriers are high), the vibrational contribution to the entropy (at -40 °C) of the TB is 23.27 cal/(mol K) while that of the BC is 22.19 cal/(mol K). This corresponds to roughly an additional 0.25 kcal/mol in favor of the TB.

The determination of the MM2* vibrational frequencies for the dimethyl silicon and 4,8-di-*tert*-butyl-substituted structure did not change the nature of the stationary points. The BB was once again characterized as a transition state. As can be seen in Table 7, substitution destabilizes the BC by 1.3 kcal/mol relative to the BB, bringing it to within 2.5 kcal/mol of the BB. The experimental observation of the BB conformer in the solid state indicates that crystal-packing forces more than compensate for this energy difference. Within the crystalline environment, the BB transition state for an isolated molecule apparently becomes a stable minimum. Moreover, the symmetry of the BB conformer may allow for a more efficient packing in the solid state. Additionally, the T transition state is most affected by substitution, being destabilized by 6.1 kcal/mol relative to the BC.

Lastly, the force field calculations fully support the contention that the pseudoequatorial preference of a methyl group on silicon or the C(12) carbon is greater than the BC–TB energy difference. For silicon substitution in the BC, the calculated preference amounts to 1.2 kcal/mol. Substitution on the C(12)methylene carbon yields a 2.6 kcal/mol calculated preference for exo substitution. Even when entropic contributions are neglected, the calculated BC–TB energy difference is 0.8 kcal/ mol.

Conclusions

The results of this study provides a rationale for understating the conformational preferences of alkyl-substituted 12*H*-dibenzo-[d,g][1,3,2]dioxasilocins. The solution, solid-state, and computational studies suggest the following conclusions regarding the conformation of the substituted 12*H*-dibenzo[d,g][1,3,2]-dioxasilocin ring system:

(1) The BB conformation is found to be a transition state for interconversion of enantiomeric TB conformations by *ab initio* calculations using a $6-31G^{**}$ split-valence plus polarization basis set. The BB conformation observed for 1 in the solid state is the result of the combination of the destabilization of the BC and crystal-packing forces. Moreover, its observation is facilitated by the ease with which the Si-O-C valence bond angle can be increased from its equilibrium value.

(2) The conformations observed in the solid-state X-ray crystal structures of 12H-dibenzo[d,g][1,3,2]dioxasilocins are sensitive to crystal-packing forces and can be different from that in solution. The extension of solid-state conformational data to solution is clearly not warranted without additional corroborating solution evidence for the 12H-dibenzo[d,g][1,3,2]-dioxasilocin ring system.

(3) In solution, the conformational preference of a particular alkyl-substituted 12H-dibenzo[d,g][1,3,2]dioxasilocin can be understood by steric arguments. In the absence of Si or C(12) substitution, a BC conformation is preferred. A monomethyl substituent on either the C(12)-bridging-methylene carbon atom or silicon of a 2,4,8,10-tetra-*tert*-butyl-substituted 12H-dibenzo-[d,g][1,3,2]dioxasilocin ring prefers a psuedoequatorial position in a BC conformation. The sterically nondemanding proton

bonded to silicon is pseudoaxially placed in the cleft between the *tert*-butyl substituents in the BC conformation. In solution, dimethyl substitution on the silicon atom of the ring forces the ring to prefer one of a family of equilibrating TB conformations to avoid the steric interactions incurred (ground-state destabilization) by pseudoaxial placement of the methyl group between the 4,8-di-tert-butyl substituents in a BC conformation. Alkyl substituents on the C(12)-carbon atom or silicon prefer exocyclic ring placement in TB conformers. The pseudoequatorial preference for a methyl substituent on either the C(12)-carbon atom or silicon is greater than the difference in energy between a BC and TB conformation in 2,4,8,10-tetra-tert-butyl-substituted 12H-dibenzo[d,g][1,3,2]dioxasilocins. In general, for these systems, the barriers to conformational interconversion (and the conformational energy differences as well) are low. As a result, many conformers can typically contribute to measured properties in solution.

(4) Both the magnitude of the ${}^{2}J_{\text{HCH}}$ geminal coupling constant of the anisochronous C(12)-methylene protons and the corresponding difference in chemical shifts ($\Delta\delta$) are indicators of the conformation in solution. Given the caveat that rapidly equilibrating populations of conformations may be present in solution, these indicators must be used with caution.

Experimental Section

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ¹H NMR (300.08 and 499.84 MHz, respectively) spectra were taken on a Varian Model Gemini-300 or Unity-500 spectrometers. All ¹H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. ²⁹Si{¹H} NMR (99.29 MHz) and ¹³C-{1H} NMR (125.70 MHz) were obtained on a Varian Model Unity-500 spectrometer. All ¹³C and ²⁹Si NMR spectra were obtained with full proton decoupling, and chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. Cr(III) acetylacetonate was added to samples in order to increase silicon relaxation rates. Low-temperature ¹H chemical shifts, J coupling constants, and NOE enhancements reported in Table 1 were conducted at -40 °C in CD2Cl2 unless indicated otherwise. Significant ¹H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets; ddq, doublet of doublets of quartets), atom assignments, coupling constant in hertz, and number of protons. Merck silica gel 60 (200-400 mesh) was used for column chromatography. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon. Elemental analyses were performed by the Analytical Research Department, Ciba Specialty Chemicals. Calculations were performed using MacroModel^{38c} version 5.0 and Spartan version 4.0 on an IBM RS/6000 model 37T.

Compounds $1,^5 2,^7 7a-c,^5$ and $7g^5$ were prepared according to literature procedures (additional previously unreported spectra data is reported on these compounds).

General Procedures for 12*H*-Dibenzo[*d*,*g*][1,3,2]dioxasilocins. Method A. To a solution of 4 mmol of the appropriate bisphenol 5 and 12 mmol of triethylamine in 10 mL of toluene or dichloromethane at 0-5 °C was added dropwise 5 mmol of the corresponding dichorosilane 6. The reaction mixture was stirred at room temperature for 2 h, and then the precipitate was removed by filtration. The solvent was removed *in vacuo*, and the residue was purified by either recrystallization or flash chromatography.

Method B. To a solution of 0.16 mol of dichorosilane **6** in 145 mL of toluene or dichloromethane at 0-5 °C was added dropwise a solution of 0.15 mol of the corresponding bisphenol **5** and 0.35 mol of triethylamine in 180 mL of toluene or dichloromethane. The reaction mixture was stirred at room temperature for 2 h, and then the precipitate

was removed by filtration. The solvent was removed *in vacuo*, and the residue was purified by either recrystallization or flash chromatography.

2,4,8,10-Tetra-*tert*-**butyl-6,6-dimethyl-12***H*-**dibenzo**[*d*,*g*][**1,3,2**]-**dioxasilocin** (**1**):^{5a} ¹³C{¹H} NMR (CDCl₃) (60 °C) δ –0.4 (s, SiCH₃), 30.4 (s), 31.5 (s), 34.2 (s), 35.0 (s), 35.2 (s), 122.4 (s), 122.6 (s), 130.7 (s), 138.4 (s),143.7 (s), 149.1 (s); ²⁹Si{¹H} NMR (CDCl₃) δ –17; ²⁹Si{¹H} NMR (CD₂Cl₂) (-40 °C) δ –6.8. Anal. Calcd for C₃₁H₄₈O₂-Si: C, 77.4; H, 10.1. Found: C, 77.0; H, 9.9.

4,8-Di-*tert*-butyl-2,6,6,10-tetramethyl-12*H*-dibenzo[*d*,*g*][1,3,2]-dioxasilocin (2):⁷ ²⁹Si{¹H} NMR (CD₂Cl₂) (-40 °C) δ -4.8.

2,2'-Methylenebis(6-*tert***-butyl-3-methylphenol) (5d).**^{41,42} Proton assignments were verified by the appropriate NOE experiments. For **5d**: ¹H NMR (CD₂Cl₂) (500 MHz) δ 1.32 (s, C(CH₃)₃,18 H), 2.40 (s, C(3)-CH₃, 6 H), 4.06 (s, CH₂, 2 H), 5.44 (s, OH, 2 H), 6.78 (d, C(4)-H, 2 H), 7.11 (d, C(5)-H, 2 H). Anal. Calcd for C₂₃H₃₂O₂: C, 81.1; H, 9.5. Found: C, 81.0; H, 9.6.

2,2'-Methylenebis(6-*tert***-butyl-3,4-dimethylphenol) (5e).^{42,43}** Proton assignments were verified by the appropriate NOE experiments. For **5e**: ¹H NMR (CD₂Cl₂) (500 MHz) δ 1.30 (s, C(CH₃)₃,18 H), 2.26 (s, C(4)-CH₃, 6 H), 2.30 (s, C(3)-CH₃, 6 H), 4.11 (s, CH₂, 2 H), 5.33 (s, OH, 2 H), 7.01 (s, C(5)-H, 2 H). Anal. Calcd for C₂₅H₃₆O₂: C, 81.5; H, 9.9. Found: C, 81.3; H, 9.9.

2,4,8,10-Tetra-tert-butyl-6-methyl-12H-dibenzo[d,g][1,3,2]dioxasilocin (7a): $5a - 13C{^{1}H}$ NMR (CDCl₃) $\delta = 0.7$ (s, SiCH₃), 30.3 (s), 31.4 (s), 34.3 (s), 34.9 (s), 122.5 (s), 125.1 (s), 132.8 (s), 139.0 (s),144.5 (s), 148.8 (s) (the C(12)-methylene carbon was not observed, which is attributed to coalescence phenomena); $^{29}Si\{^1H\}$ NMR (CDCl₃) $(-40 \text{ °C}) \delta - 19.4$ (major conformation). Anal. Calcd for C₃₀H₄₆O₂-Si: C, 77.2; H, 9.9. Found: C, 77.2; H, 9.7. Suitable crystals for X-ray analysis were grown from acetonitrile. Crystal data for 7a: $C_{30}H_{46}O_2Si$; formula weight (g mol) = 466.79; crystal size (mm) 0.46 $\times 0.28 \times 0.15$; triclinic; cell parameters a = 12.921(2) Å, b = 11.064-(2) Å, c = 10.876 Å, $\alpha = 103.76(1)^{\circ}$, $\beta = 77.26(1)^{\circ}$, $\gamma = 102.99(1)^{\circ}$, V = 1448.4(6) Å³; space group = $P\overline{1}$; $d_{calcd} = 1.070$ Mg m⁻³, Z = 2; data collection Philips PW1100 diffractometer; Mo K α ($\lambda = 0.7107$ Å) radiation; graphite monochromator; scan type $2\theta - \theta$; 2θ range = $6-42^{\circ}$; observed reflections 1930 ($I > 3.0\sigma(I)$); number of parameters 482; *R* indices R = 0.068, $R_w = 0.076$; refinement method full-matrix; hydrogen atoms located, not refined; maximum density in final difference map (e Å⁻³) 0.341; Siemens SHELXTL.

2,4,8,10-Tetra-tert-butyl-6,12-dimethyl-12H-dibenzo[d,g][1,3,2]dioxasilocin (7b).^{5a} Method A: toluene solvent; 98.9% yield; cis/ trans ratio = 77:23; recrystallization from a 1:1 mixture of toluene/ acetonitrile gave 7b (79.5%) with a cis/trans ratio = 78:22. For trans-**7b**: ²⁹Si{¹H} NMR (CD₂Cl₂) (-40 °C) δ -19.4. For *cis*-**7b**: ²⁹Si{¹H} NMR (CDCl₃) (-40 °C) δ -27.0. Anal. Calcd for C₃₁H₄₈O₂Si: C, 77.4; H, 10.1; Si, 5.8. Found: C, 77.3; H, 9.9; Si, 5.9. Method B: toluene solvent; 96.7% yield; cis/trans ratio = 55:45. Flash chromatography (hexane/ethyl acetate 19:1) gave trans-7b (24%); mp 213-214 °C. Anal. Calcd for C31H48O2Si: C, 77.4; H, 10.1; Si, 5.8. Found: C, 77.4; H, 10.0; Si, 5.8. Suitable crystals for X-ray analysis were grown from acetone. Crystal data for 7b: C₃₁H₄₈O₂Si; formula weight (g mol) = 480.80; crystal size (mm) $0.76 \times 0.52 \times 0.15$; triclinic; cell parameters a = 13.491(1) Å, b = 11.315(2) Å, c = 10.476Å, $\alpha = 99.10(1)^{\circ}$, $\beta = 103.19(1)^{\circ}$, $\gamma = 80.81(1)^{\circ}$, V = 1524.6(6) Å³; space group = $P\overline{1}$; $d_{calcd} = 1.047 \text{ Mg m}^{-3}$, Z = 2; data collection Philips PW1100 diffractometer; Mo K α ($\lambda = 0.7107$ Å) radiation; graphite monochromator; scan type $2\theta - \theta$; 2θ range = $6-54^{\circ}$; observed reflections 4505 ($I > 3.0\sigma(I)$); number of parameters 307; R indices R = 0.058, $R_{\rm w}$ = 0.066; refinement method full-matrix; hydrogen atoms located, not refined; maximum density in final difference map (e $Å^{-3}$) 0.311; Siemens SHELXTL.

2,4,8,10-Tetra-*tert*-butyl-6,6,12-trimethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin (7c):^{5a} ²⁹Si{¹H} NMR (CDCl₃) (-40 °C) δ -7.1. Anal. Calcd for C₃₂H₅₀O₂Si: C, 77.7; H, 10.2. Found: C, 77.5; H, 9.9. Suitable crystals for X-ray analysis were grown from acetone. Crystal data for 7c: C₃₂H₅₀O₂Si; formula weight (g mol) = 494.83; crystal size (mm) 0.45 × 0.29 × 0.15; monoclinic; cell parameters *a* = 26.884-(3) Å, *b* = 22.156(2) Å, *c* = 10.792 Å, β = 99.21(1)°, *V* = 6345(1) Å³; space group = *P*2₁/*n*; *d*_{calcd} = 1.036 Mg m⁻³, *Z* = 8; data collection Philips PW1100 diffractometer; Mo K α (λ = 0.7107 Å) radiation; graphite monochromator; scan type $2\theta - \theta$; 2θ range = 6-40°; observed reflections 2500 (*I* > 3.0 σ (*I*)); number of parameters 631; *R* indices *R* = 0.072, *R*_w = 0.079; refinement method full-matrix; hydrogen atoms located, not refined; maximum density in final difference map (e Å⁻³) 0.544; Siemens SHELXTL.

4,8-Di-tert-butyl-1,11,6,6-tetramethyl-12H-dibenzo[d,g][1,3,2]dioxasilocin (7d). Method A: dichloromethane solvent; flash chromatography (hexane) gave a white solid (88.7%), mp 124-126 °C; ²⁹Si{¹H} NMR (CDCl₃) (-40 °C) δ -4.2. Anal. Calcd for C₂₅H₃₆O₂-Si: C, 75.7; H, 9.2; Si, 7.1. Found: C, 75.7; H, 9.1; Si, 7.3. Suitable crystals for X-ray analysis were grown from acetone. Crystal data for **7d**: $C_{25}H_{36}O_2S_i$; formula weight (g mol) = 396.64; crystal size (mm) $0.76 \times 0.41 \times 0.11$; monoclinic; cell parameters a = 13.997(2) Å, b = 6.428(1) Å, c = 26.490(2) Å, $\beta = 98.30(1)^{\circ}$, V = 2358.4(6) Å³; space group = $P2_1/c$; $d_{calcd} = 1.117$ Mg m⁻³, Z = 4; data collection Philips PW1100 diffractometer; Mo K α ($\lambda = 0.7107$ Å) radiation; graphite monochromator; scan type $2\theta - \theta$; 2θ range = $6-50^{\circ}$; observed reflections 2337 ($I > 3.0\sigma(I)$); number of parameters 253; R indices R = 0.038, $R_w = 0.045$; refinement method full-matrix; hydrogen atoms located, not refined; maximum density in final difference map (e Å⁻³) 0.231; Siemens SHELXTL.

4,8-Di-*tert*-butyl-1,2,10,11,6,6-hexamethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin (7e). Method A: dichloromethane solvent; flash chromatography (hexane) gave a white solid (77.3%), mp 133–136 °C; ²⁹Si{¹H} NMR (CDCl₃) (-40 °C) δ -4.4. Anal. Calcd for C₂₇H₄₀O₂-Si: C, 76.4; H, 9.5; Si, 6.6. Found: C, 76.3; H, 9.4; Si, 6.7.

4,8-Di-*tert*-**butyl-1,2,10,11,6-pentamethyl-12***H*-**dibenzo**[*d*,*g*][**1,3,2]**-**dioxasilocin (7f). Method A:** dichloromethane solvent; bulb-to-bulb distillation to give a white solid (69 %), mp 140–147 °C; bp 180–190 °C (0.001 Torr); ²⁹Si{¹H} NMR (CDCl₃) (-40 °C) δ –18.3 (minor), –18.8 (major). Anal. Calcd for C₂₇H₄₀O₂Si: C, 76.0; H, 9.3; Si, 6.8. Found: C, 75.8; H, 9.5; Si, 6.7.

2,4,8,10-Tetra-*tert*-**butyl**-**12***H*-**dibenzo**[*d*,*g*][**1,3,2**]**dioxasilocin** (**7g**):^{5a} ¹H NMR (C₂D₂Cl₄) (110 °C) δ 1.32 (s, 18 H), 1.41 (s, 18 H), 3.92 (s, CH₂, 2 H), 5.03 (s, SiH₂, 2 H), 7.21 (unresolved d, 2 H), 7.24 (unresolved d, 2 H); ¹H NMR (CD₂Cl₂) (-95 °C) δ 1.22 (s, 18 H), 1.29 (s, 18 H), 3.42 (d, CH₂, ²*J*_{HCH} = 13.4 Hz, 1 H), 4.28 (d, CH₂, ²*J*_{HCH} = 13.4 Hz, 1 H), 4.28 (d, CH₂, ²*J*_{HCH} = 13.4 Hz, 1 H), 5.07 (d, SiH₂, ²*J*_{HSiH} = 27.3 Hz, 1 H), 7.13 (d, 2 H), 7.26 (d, 2 H); exact mass calcd for C₂₉H₄₄O₂Si 452.3111, found 452.3158.

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Supporting Information Available: Data from X-ray crystallographic analysis of the 12*H*-dibenzo[d,g][1,3,2]dioxasilocins 1, 7b_{trans}, 7c, 7d, and 7a_{major} including crystal data, bond angles, bond lengths, and atomic parameters; Figure 8; and Table 4 (28 pages). See any current masthead for ordering and Internet access instructions.

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